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(21) International Application Number: PCT/NL91/00219 (22) International Filing Date: 7 November 1991 (07.11.91) (30) Priority data: 610,050 7 November 1990 (07.11.90) US (71) Applicant: DSM N.V [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors: MURRAY, Kevin, P. ; 1759 Glen Lake Road, Hoffman Estates, IL 60195 (US). CHAWLA, Chander, P. ; 716 Independence #3, Palatine, IL 60074 (US). POKLACKI, Erwin, S. ; 1223 South Fernandez, Arlington Heights, IL 60005 (US).		(74) Agent: DEN HARTOG, Jeroen, Hendrikus, Joseph; DSM N.V., Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: NOVEL ANTIOXIDANT AND LIGHT STABILIZER BOUND OLIGOMER SYSTEMS FOR RADIATION CURED MATERIALS (57) Abstract The performance of ultraviolet light cured coatings may be enhanced through the addition of covalently bound light stabilizer and antioxidant so that the cured films are not subject to degradation or yellowing.		

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**"NOVEL ANTIOXIDANT AND LIGHT
STABILIZER BOUND OLIGOMER
SYSTEMS FOR RADIATION CURED MATERIALS"**

5 Background of the Invention

 The need to stabilize radiation cured coatings
(actinic light or ionizing radiation) to the effects of
long term exposure to light and oxygen is well known.
The need, for example, for non-yellowing light cured
10 varnishes on medicinal or cosmetic labels is imperative.
Any tendency toward yellowing is interpreted by the
consumer that the contents are in some way old and not
as efficacious. This creates a serious problem with
store displays. Similarly, ultraviolet coatings on
15 floor tile must not yellow on exposure to sunlight over
long periods of time. Such failure is normally seen as a
yellowing of the tile near windows or doors with a
gradation to colorless as the distance from the window
increases.

20 U.S. Patent No. 4,344,830 discloses the
incorporation of hydroxy benzotriazoles in ultraviolet
light curable coatings to impart weathering resistance
to plastic substrates. These materials were simply
admixed with the coating composition and did not react
25 to become part of the polymer.

 U.S. Patent No. 4,355,071 discloses the
preparation of clear ultraviolet light curable coatings
over a pigmented coating which contains about 1 + 20%,
based on the weight of the binder, of ultraviolet light
30 stabilizers. The stabilizer is not incorporated in the
ultraviolet light curable clear top coat and does not
interfere with the cure speed. However, upon curing the
stabilizer is free to migrate into the clear top coat to
provide protection from discoloration.

35 The idea of incorporating the light stabilizer
into the polymer is disclosed in U.S. Patent No.
4,504,628. A stabilizer with a functional group is

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reacted with a compound having both isocyanate and polymerizable vinyl groups to produce a new monomer. Upon polymerization of compositions containing this new monomer, the stabilizer becomes an integral part of the polymer and is no longer fugitive or extractable. An example of this type of structure might be the reaction product of a hydroxy functional hindered amine stabilizer with isocyanatoethyl methacrylate. Other examples of this type of product are the reaction product of isophorone diisocyanate or toluene diisocyanate with one mole of the stabilizer and one mole of hydroxyethyl acrylate. These monomers may have a high order of volatility, toxicity, and possibly a less desirable rate of polymerization. In addition, complying with all of the regulations of the Environmental Protection Agency for the introduction of new monomers into commerce can involve prohibitive associated costs.

Summary of the Invention

The present invention relates to a compound containing at least one polymerizable ethylenically unsaturated functional group and at least one stabilizer moiety covalently bonded within.

More particularly, the present invention relates to a polyurethane having at least one ethylenically unsaturated functional group and at least one stabilizer moiety, said urethane having a number average molecular weight of 1,000 to 10,000 daltons and being the reaction product of an isocyanate terminated prepolymer having a number average molecular weight of about 500 to 4,000 daltons, an equimolar mixture of a hydroxy terminated ethylenically unsaturated monomer and stabilizer compounds having a functional group capable of reacting with the isocyanate moiety.

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Preferably the stabilizer is N-(2,2,6,6-tetramethyl-4-piperidiny1)-N-hydroxybenzen pr pionic hydrazide or 3,5-ditertiary butyl-4-hydroxybenzenepropionic hydrazide, alone or in combination and the hydroxy functional ethylenically unsaturated monomer is taken from the classes of acrylates, methacrylates, acrylamides, methacrylamides, maleates and vinyl ethers.

The present invention is also directed to a coating composition that comprises: (i) about 10 to about 90% weight percent based on total weight of the coating composition, of an unsaturated polyurethane having a number average molecular weight of about 1,000 to about 10,000 daltons, being the reaction product of a prepolymer having a number average molecular weight of about 400 to about 2,000 daltons, a diisocyanate and a hydroxy functional unsaturated monomer, (ii) about 0.01 to about 25 weight percent, based on total weight of the coating composition, of a polyurethane having on at least one end an unsaturated moiety and on another end, the bound antioxidant, having a number average molecular weight of about 1,000 to about 10,000 daltons being the reaction product of an isocyanate terminated prepolymer having a number average molecular weight of about 500 to about 4,000 daltons, on equimolar mixture of hydroxy functional unsaturated monomer and an antioxidant containing a functional group capable of reacting with an isocyanate, (iii) about 0.01 to about 25 weight percent, based on the total weight of the coating composition of a polyurethane having on at least one end an ethylenically unsaturated group and on another, a bound light stabilizer moiety having a number average molecular weight of about 1,000 to about 10,000 daltons being the reaction product of an isocyanate terminated prepolymer having a number average molecular weight of

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about 500 to about 4,000 daltons, an equimolar mixture
of hydroxy functional thylenically unsaturated monomer
and a light stabilizing compound having a functional
group capable of reacting with an isocyanate group; and
5 (IV) about 5 to about 80 weight percent, based on the
total weight of the coating composition, of at least one
saturated compound that optionally further comprises a
photoinitiator.

It has been found that the compositions of the
10 present invention that contain bound light stabilizers
and bound antioxidants produce cured coatings which have
superior stability without being subject to a loss of
these properties by extraction with water or solvents.
The antioxidant and light stabilization benefits were
15 permanent properties of the cured films. The stabilizer
containing oligomers, since they have polymerizable
functional groups only on one end, are bulky monomeric
materials which also function as internal plasticizers;
that is, they are capable of inhibiting crystallization
20 of polymer chains.

The acrylated polyurethane and the oligomer
bound stabilizers are produced sequentially in situ with
the acrylated polyurethane being the first to be
produced.

25 Conventional photoinitiators can also be
present in the compositions of the present invention to
initiate polymerization by ultraviolet light and visible
light near the ultraviolet wavelength range. The
compositions of the present invention will also
30 polymerize in the absence of photoinitiators by the
influence of ionizing radiation such as produced by an
electron beam machine. Similarly, these compositions
may also be polymerized thermally with appropriate
thermal free radical initiators, e.g. azobis

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isobutyronitrile, benzoyl peroxide, r vari us
hydroperoxides.

Detailed Description of the Preferred Embodiments

5 Although this invention is susceptible to
embodiment in many different forms, preferred
embodiments of this invention are shown. It should be
understood, however, that the present disclosure is to
10 be considered as an exemplification of the principles of
the invention and is not intended to limit the invention
to embodiments illustrated.

 Oligomeric structures useful in radiation
curable coatings, either actinic or ionizing, which
provide the benefits of antioxidants and light
15 stabilizers but without their undesirable
extractabilities are disclosed. These oligomeric
structures comprise a polyurethane which contains
(meth)acrylate groups and at least one bound stabilizer
group, which is attached through a urethane or urea
20 linkage. In practice, two oligomeric structures, one
containing an antioxidant moiety and the other a light
stabilizing moiety are prepared and used in admixture.
These oligomers are used at a 0.01 to 25 weight percent
level with oligomers which are totally (meth)acrylated.
25 Further, these oligomers have a number average molecular
weight of about 1,000 to 10,000 daltons.

 The term "dalton", in its various grammatical
forms, defines a unit of mass that is 1/12th the mass of
carbon-12.

30 The term "(meth)acrylate", and various
grammatical forms thereof, identifies esters that are
the reaction product of acrylic or methacrylic acid with
a hydroxy group-containing compound.

 The (meth)acrylate-terminated polyurethane is
35 the reaction product of a prepolymer, an organic

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diis cyanate and a hydroxy (meth)acrylate. The stabilizing ligomers are reaction products of a prepolymer, organic diisocyanates, a hydroxy (meth)acrylate, and a stabilizing compound.

5 The prepolymer has a carbon chain that can comprise oxygen and/or nitrogen atoms to which the terminal (meth)acrylate functionality is added by use of the diisocyanate. Selection of the prepolymer can affect the physical properties of the coatings produced from the oligomer-containing composition.

10 The prepolymer has on average at least about two prepolymer functional groups that are reactive with the isocyanate group, e.g., a hydroxy, mercapto, amine or similar group which has a reactive protonic group. 15 Presently, the preferred prepolymer functional group is a hydroxy group.

 The number average molecular weight of the prepolymer is about 500 to about 4,000, preferably about 800 to about 2,500, daltons.

20 Prepolymers are selected from the group consisting of hydroxy or amine terminated polycarbonates, polyesters, polyethers, unsaturated and hydrogenated polybutadienes, polysiloxanes, Bisphenol A-Alkoxylates, fluorinated derivatives of these and 25 mixtures thereof. The reaction of the polyols with the diisocyanate may be conducted so as to simply end cap the hydroxyl groups with isocyanate groups, or to also produce chain extended structures which are isocyanate terminated.

30 The polycarbonate diols are conventionally produced by the alcoholysis of diethylene carbonate with a diol. The diol is an alkylene diol having about 2 to about 12 carbon atoms, e.g., 1,4-butane diol, 1,6-hexane diol, 1,12-dodecane diol and the like. Mixtures of 35 these diols can also be utilized. The polycarbonate

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diol can contain ether linkages in the backbone in addition to carbonate groups. Thus polycarbonate copolymers of alkylene oxide monomers and the previously described alkylene ether diols are suitable. Suitable alkylene oxide monomers include triethylene glycol and tripropylene glycol, tetrahydrofuran and the like. Mixtures of the polycarbonate diols and polycarbonate copolymer diols can also be utilized.

Suitable polycarbonate diols include Duracarb 122, commercially available from PPG Industries and Permanol KM10-1733, commercially available from Permuthane, Inc., Ma. Durocarb 122 is produced by the alcoholysis of diethylcarbonate with hexane diol.

Illustrative polyesters include the reaction products of saturated polycarboxylic acids, or their anhydrides, and diols. Suitable saturated polycarboxylic acids and anhydrides include phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, tetrachlorophthalic acid, adipic acid, azelaic acid, sebacic acid, succinic acid, glutaric acid, malonic acid, pimelic acid, suberic acid, 2,2-dimethylsuccinic acid, 3,3-dimethylglutaric acid, 2,2-dimethylsuccinic acid, 3,3-dimethylglutaric acid, 2,2-dimethylglutaric acid, the like, anhydrides thereof and mixtures thereof. Suitable diols include 1,4-butanediol, 1,8-octane diol, diethylene glycol, 1,6-hexane diol, dimethylol cyclohexane, and the like. Included in this classification are the polycaprolactones, commercially available from Union Carbide under the trade designation Tone Polyol series of products, e.g., Tone 0200, 0221, 0301, 0310, 2201, and 2221. Tone Polyol 0301 and 0310 are trifunctional.

Representatives of the polyether diols are those formed from the polymerization of alkylene oxides

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such as poly (pr pylene oxide), commercially available from Uni n Carbide under the trade designation Niox PPG 1025 and poly (tetramethylene glycol), commercially available from DuPont under the trade designation
5 Terathane 1000.

The alkyl substituted poly(tetrahydrofurans) have ring structures that open during polymerization to produce hydroxy terminated polyethers which may be used to make the polymer bound stabilizers of this invention.
10 The alkyl group of the alkyl substituted poly(tetrahydrofurans) has about 1 to about 4 carbon atoms. Representative of the alkyl substituted poly(tetrahydrofurans) is poly(3-methyltetrahydrofuran). Representative of the cyclic ethers with which the alkyl
15 substituted tetrahydrofurans can be copolymerized are ethylene oxide, propylene oxide, tetrahydrofuran and the like.

Representative of the Bisphenol-A alkoxyates are those wherein the alkoxy group contains about 2 to
20 about 4 carbon atoms, e.g., ethoxy. A commercial Bisphenol-A alkoxyate is the Bisphenol-A diethoxyate available under the trade designation Dianol 22 from Akzo Research, The Netherlands.

Representative of siloxanes is
25 poly(dimethylsiloxane) commercially available from Dow Corning under the trade designation DC 193.

Representative of the hydrogenated polybutadiene prepolymers are materials made from butadiene monomers that have a high percentage of 1,2
30 vinyl structure, are terminated with hydroxyl groups, and are hydrogenated until essentially no unsaturation remains. Such a material is commercially available from Nippon Soda Ltd. through Nissho Iwai, New York, NY as Nisso PB. GI-1000.

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The fluorinated prepolymers are represented by polyethers based on perfluorinated poly(ethylene oxide) in which the fluorine atoms are in the main chain.

5 Examples of such fluorinated prepolymers include Fomblin Z-DOL-TX from Ausimont, Morristown, N.J. and MDP 5992 from DuPont, Wilmington, Del., a polyether with perfluoroalkyl groups pendant to the main chain.

Any of a wide variety of organic polyisocyanates, alone or in admixture, can be utilized. 10 Representative diisocyanates include isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HMDI), cyclohexylene diisocyanate, methylene dicyclohexane diisocyanate, 2,2,4-trimethyl 15 hexamethylene diisocyanate, m-phenylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,10-decamethylene diisocyanate, 1,4-cyclohexylene diisocyanate, and polyalkyloxide and 20 polyester glycol diisocyanates such as polytetramethylene ether glycol terminated with TDI and polyethylene adipate terminated with TDI, respectively.

The hydroxy(meth)acrylate can be a 25 mono(meth)acrylate or a poly(meth)acrylate. Monohydric monoacrylates are presently preferred. The reaction of the isocyanate group with a hydroxy group of the hydroxy(meth)acrylate produces a urethane linkage which results in the formation of a (meth)acrylate terminated 30 urethane.

Suitable monohydric acrylates are the C₂-C₄ alkyl acrylates and polyacrylates. Illustrative of these acrylates are 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, glyceryl diacrylate, and the 35 like. Mixtures of these acrylates are also suitable.

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The methacrylat counterparts of the above acrylat s can also be utilized.

5 The reactive stabilizers which are preferred are: Luchem HA-R100, N-(2,2,6,6-tetramethyl-4-piperidinyl)-N-aminooxamide and Luchem AOR-300, 3,5-di-tertiary butyl-4-hydroxybenzenepropionic hydrazide. These materials are available from ATOCHEM North America Inc. The N-amino group of both of these compounds is very reactive towards isocyanates and therefore is used
10 to bind the stabilizers to the oligomer covalently. Other reactive UV light stabilizers and antioxidants which have hydroxyl, mercapto, or amino groups may also be used to produce a polymer-bound stabilizer system.

In practice, the oligomers are produced first
15 by the reaction of a diisocyanate with the hydroxy alkyl meth(acrylate). To facilitate the mixing of the viscous mixture, a monoacrylate ester of low viscosity is used as a solvent for the reaction, e.g. vinyl pyrrolidone or octadecyl acrylate. To facilitate the reaction of the
20 isocyanate to produce urethanes, a catalyst is included, e.g., about 0.01 to about 0.3, preferably about 0.04 percent of dibutyltin dilaurate is used. The above reaction product is next reacted with the hydroxy terminated prepolymer. The stoichiometry is so adjusted
25 that there are unreacted isocyanate groups remaining on some of the oligomer molecules. The stabilizing oligomers are then produced, in situ, by reacting the remaining free isocyanate groups with a stoichiometric amount of the stabilizers.

30 Formulation of the coating is usually accomplished in the same vessel as was used for the reaction of the preceding paragraph. Diluent monomers, photoinitiators, stabilizers, adhesion promoters, and the like are added to the oligomer mixture.

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Preferred photoinitiators are (1) hydroxy-alkoxy-functional acetophenone derivatives, more preferably hydroxyalkyl phenones, and (2) benzoyl diaryl phosphine oxides. One commercially available compound is the Ciba-Geigy product CGI-369 which is 2-benzyl-dimethylamino-1-4-morpholine phenyl)-butanone-1. Irgacure 184, also from Ciba-Geigy, is another useful acetophenone derivative and has the structure: a-hydroxycyclohexyl phenyl ketone. Still another commercially useful acetophenone derivative is diethoxy acetophenone which is available from Upjohn Chemicals. An example of the phosphine oxide type photoinitiator is 2,4,6-trimethyl benzoyl diphenyl phosphine oxide which is commercially available from BASF under the trade designation Lucirin TPO. This list of photoinitiators is incomplete. However, additional commercially available materials are well known to those skilled in the art.

The present invention will be illustrated by the following representative examples.

EXAMPLE 1.

An additive bound oligomer of the present invention was prepared in a 2000 milliliter (ml), 4 neck flask that was equipped with a variable speed paddle stirrer, dry air inlet, thermometer and condenser. Provision was made to heat or cool the flask. A dry air sparge of the flask was initiated. The flask was charged with 186.9 gms. (0.8374 moles) of isophorone diisocyanate (IPDI¹), 150 gms. of octyl/decyl acrylate (ODA²) as a diluent, 0.30 gms. of phenothiazine³ (radical inhibitor) and 0.70 gms. of dibutyltindilaurate (DBTDL⁴) (urethane catalyst).

Next charged to the flask over a period of 1/2 hour while the temperature was maintained below 40°C,

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was 45.8 gms. (0.3944 moles) of hydroxy ethyl acrylate (HEA)⁵. The contents were stirred at 40°C for one hour to allow sufficient time for all of the HEA to react with the IPDI. The progress of the reaction was
5 determined by a standard procedure of treating an aliquot of the reaction mixture with an excess of dibutylamine and then backtitrating the excess dibutylamine with dilute standard HCl solution.

The flask was next charged with 531 gms.
10 (0.5783 moles) of an aliphatic polycarbonate diol (Permanol KM-10-1733⁶) blended with 8.71 g (0.0298 moles) of 3,5-ditertiary butyl-4-hydroxy benzene propionic hydrazide (Luchem AOR 300)⁷ over a period of fifteen minutes and the temperature was increased to
15 70°C. To the reaction mixture was added an additional 43.0 gms. of ODA for a total of 20% diluent. The reaction contents were stirred at 70°C for eight hours to ensure the complete reaction of the polycarbonate diol. The % unreacted isocyanate groups were determined
20 to ensure that all of the IPDI and the IPDI-HEA had been incorporated into the oligomer.

Next charged into the reactor was 8.71 gms. (0.0298 moles) of finely powdered 3,5-ditertiary butyl-4-hydroxybenzene propionic hydrazide (Luchem AOR 300)
25 and 8.48 gms (0.0350 moles) of finely powdered N-(2,2,6,6-tetramethyl-4-piperdiny)-N-amino oxamide (Luchem HA-R100)⁸. The addition of these last two reagents took 20 minutes. The reaction mixture was stirred at 70°C for two and a half hours and then the
30 temperature was increased to 90°C. The contents were stirred at 90°C for one hour and forty minutes. An aliquot indicated essentially no isocyanate functionality left and the heating was stopped.

The additive bound oligomer was admixed with
35 the diluent monomers Aronix M-113⁹ and V-Pyrole¹⁰,

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adhesion promoter (MEMO)¹¹ and the photoinitiator CGI-369¹² in a weight ratio of oligomer:Aronix M-113:V-Pyrole:MEMO:CGI-369 of about 59.8: 34: 4.1: 1: 1 to produce a liquid composition of the invention.

5 The liquid composition was drawn down as a film on a glass plate and cured using a "D" Lamp from Fusion Curing Systems, Rockville, MD. The "D" Lamp emits actinic energy having a wave length of about 200 to about 470nm, with the peak actinic energy being about
10 380 nm and a power output of about 300 watts per linear inch. The cured film showed non-extractability of the additives.

- 15 1.) IPDI, isophorone diisocyanate, commercially available from Huls America, Nuodex Inc. Piscataway, N.J..
- 2.) ODA, octyl/decyl acrylate, commercially available from Radcure Specialties, Louisville, KY.
- 20 3.) Phenothiazine, commercially available from ICI, Wilmington Delaware.
- 4.) DBTDL, dibutyltin dilaurate, commercially available from Mooney Chemical Co.
- 5.) HEA, hydroxyethyl acrylate, commercially available from Dow Chemical Co., Midland Michigan.
- 25 6.) Permanol KM-1--1733, commercially available from Permuthane Coatings, Peabody, MA.
- 7.) Luchem AOR 300, commercially available from the Lucidol division of the Pennwalt Corporation, Buffalo N.Y.
- 30 8.) Luchem HA-R100, commercially available from the Lucidol division of the Pennwalt Corporation, Buffalo N. Y.
- 9.) Aronix M-113, ethoxylated nonylphenol acrylate, commercially available from Tao Gosei Chemical Industry
35 C . Ltd. Japan

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10.) V-Pyr 1e, commercially available from GAF Corporation, New York, N.Y..

11.) MEMO, gamma-methacryloxypropyltrimethoxysilane, commercially available from Huls, Bristol Pa.

5 12.) CGI-369, 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-butanone-1, commercially available from Ciba Geigy, Ardsley, NY.

EXAMPLE 2.

10 In a second formulated composition, the bound oligomer of Example 1. was admixed with the diluent monomer Aronix M-113, adhesion promoter (MEMO) and the photoinitiator Lucirin TPO in a weight ratio of
15 oligomer:Aronix M-113:MEMO:Lucirin TPO¹³ about 53.2:43.6:1.1:2.1. The liquid composition was drawn down on a glass plate as a film and cured using the "D" lamp. The cured film was immersed in acetone for 24 hours and dried. The dried film was placed in a Dupont 912 Differential Scanning Calorimeter and heated at a
20 rate of 10°C/ minute. The temperature at which exothermic decomposition occurs (oxidation induction temperature or OIT) was recorded. The value obtained was about the same (257°C for control and 264°C after 24 hours immersion in acetone), the unextracted cured film
25 demonstrating the non-extractability of the stabilizer system. Thermogravimetric analysis (TGA)¹⁴ showed very little weight loss (-1.1%) on heating at 200°C for forty minutes. An analysis of the oligomer showed that both the additives were bound to the oligomer backbone.

30

13.) Lucirin TPO, 2,4,6-trimethylbenzoyl diphenyl phosphine oxide, commercially available from BASF Corporation Germany.

35 14.) TGA conducted on a DuPont 951 Thermogravimetric Analysis Instrument.

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EXAMPLE 3.

The following composition was prepared as a control. A similar oligomer based on HEA/IPDI/PERMANOL/IPDI/HEA was prepared without any bound additives. The composition contained 57% oligomer, 33% Aronix M-113, 4% V-Pyrole, 4% Irgacure 184¹⁵, 1% MEMO, 0.5% Tinuvin 770¹⁶, and 0.5% Irganox 1035¹⁷.

The sample was cured as in Example 1 and extracted with acetone. Differential scanning calorimetry gave a reduction in OIT of 40°C as compared with the OIT of the unextracted film. The Thermogravimetric Analysis gave a weight loss of 4.4% for the acetone extracted film.

15.) Irgacure 184, 1-hydroxycyclohexyl phenyl ketone, commercially available from Ciba Geigy, Ardsley NY.

16.) Tinuvin 770, Bis (2,2,6,6-tetramethyl-4-piperdiny1) sebacate, commercially available from Ciba Geigy.

17.) Irganox 1035, thiodiethylene bis-(3,5-di-tertiarybutyl-4-hydroxy) hydrocinnamate, commercially available from Ciba Geigy.

EXAMPLE 4.

An antioxidant bound oligomer of the present invention was prepared utilizing a flask as described in Example 1 that was charged with 186.89 gms (0.8375 moles) of isophoronediiisocyanate (IPDI), 150.15 gms of octyl/decyl acrylate (ODA), 0.30 gms phenothiazine and 0.60 gms of dibutyltindilaurate (DBTDL). The dry air sparge was started from the beginning of the addition to the flask. To the mixture in the flask was added over a period of one half hour 49.44 gms. (0.4258) moles of hydroxyethyl acrylate (HEA), during which time the temperature was maintained below 40°C. The contents

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were stirred at 40°C for one hour to allow sufficient time for the HEA to react completely with the IPDI. At this time, the free isocyanate % was determined as described in Example 1.

5 The temperature was increased to 70°C while 541.97 gms (1.181 moles) of Permanol KM10-1733 blended with 8.7 gms (0.0298 moles) of Luchem AOR 300⁷ was added over a period of fifteen minutes. An additional 47.15 gms of ODA was added to the reaction mixture. The
10 contents of the reaction mixture were stirred for ten hours at 70°C. An aliquot sample showed essentially all of the IPDI had reacted.

 The antioxidant bound oligomer was admixed with the diluent monomers Aronix M-113 and V-Pyrole,
15 adhesion promoter (MEMO), Tinuvin 770, and the photoinitiator CGI-369 in a ratio of about 59.3:34:4:1.0:0.5:1.0 to produce a liquid composition of the invention. A film of the composition was cured
20 using the "D" Lamp. The cured film showed non-extractability of the additive. An analysis of the oligomer showed that the additive was bound to the oligomer.

EXAMPLE 5.

25 A light stabilizer bound oligomer of the present invention was prepared utilizing a flask described in Example 1 that was charged with 186.89 g (0.8375 moles) of isophorondiisocyanate (IPDI), 150.15 g of octyl/decyl acrylate (ODA), 0.30 g of phenothiazine
30 and 0.60 g of dibutyltindilaurate (DBTDL). The air sparge was started from the beginning of the addition to the flask. 47.02 g (0.4049 moles) of hydroxy ethyl acrylate (HEA) was added to the reaction mixture over a
35 period of a half hour, during which time the temperature was maintained below 40°C. The contents were stirred at

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40°C for 1 hour to allow sufficient time for HEA to react with IPDI. At this time, the amount of remaining NCO groups was determined by a standard procedure of backtitrating excess dibutylamine with dilute HCl solution.

5 The temperature of the reaction mixture was increased to 70°C and 540.06 g (0.5882 moles) of an aliphatic polycarbonate diol (Permanol KM10-1733) was added to it over a period of 15 minutes. The reaction contents were stirred at 70°C for 8 hours to allow sufficient time for the reaction of polycarbonate diol hydroxy groups to react with the isocyanate groups. At 10 this time, percent NCO was determined. 5.99 g (0.0247 moles) of N-(2,2,6,6-tetramethyl-4-piperdiny)-N-amino oxamide (Luchem HA-R100) was added to the reaction 15 mixture over a period of 10 minutes. An additional 44.99 g of ODA was added to the reaction mixture. The reaction temperature was increased to 90°C and the contents were stirred for seven and a half hours. An 20 aliquot sample indicated essentially no isocyanate functionality remaining and heating was stopped. The material was poured out of the reaction vessel into a container.

The light stabilizer bound oligomer was 25 admixed with the diluent monomers Aronix M-113 and V-Pyrol, adhesion promoter (MEMO), Irganox 1035 and the photoinitiator CGI-369 from Ciba-Geigy in a weight ratio of oligomer: Aronix M-113: V-Pyrol: MEMO: Irganox 1035: CGI-369 about 59.2:34.1:4.1:1.0:0.5:1.0 to produce a 30 liquid composition of the invention. A film of this composition was cured using the "D" lamp. The cured film showed non-extractability of the light stabilizer. An analysis of the oligomer showed that the additive was bound to the oligomer backbone.

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EXAMPLE 6.

Another additive bound ligand of the present invention was prepared utilizing a flask as described in Example 1 that was charged with 187.79 g (0.8375 moles) of isophorondiisocyanate (IPDI), 150.05 g of octyl/decyl acrylate (ODA), 0.30 g of phenothiazine and 0.61 g of dibutyltin dilaurate (DBTDL). The air sparge was started from the beginning of the addition to the flask. 45.30 g (0.3901 moles) of hydroxy ethyl acrylate (HEA) was added to the reaction mixture over a period of a 1/2 hour during which time the temperature was maintained below 40°C. The reaction contents were stirred at 40°C for 1 hour to allow sufficient time for HEA to reach with IPDI. At this time, the amount of remaining NCO groups was determined by a standard procedure of backtitrating excess dibutylamine with dilute HCl solution.

The temperature of the reaction mixture was increased to 70°C and 521.35 g (0.5678 moles) of an aliphatic polycarbonate diol (Permanol km10-1733) was added to it over a period of 10-15 minutes. The reaction contents were stirred at 70°C for 8 hours to allow sufficient time for the reaction of polycarbonate diol hydroxy groups to react with the isocyanate groups. 8.71 g (0.0298 moles) of 3,5-ditertiary butyl-4-hydroxybenzene propionic hydrazide (Luchem AOR 300) was added to the reaction mixture followed by the addition of 39.80 g of ODA. The reaction contents were stirred for one and a half hours at 70°C. At this time a sample for percent NCO was taken. 8.71 g (0.0359 moles) of N-(2,2,6,6-tetramethyl-4-piperidyl)-N-aminooxamide (Luchem HA-R100) was added over a period of 10 minutes followed by the addition of 59.50 g ODA. The reaction mixture was stirred for 2 hours at 70°C and then the temperature was increased to 80°C. After 1/2 hour of

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stirring at 80°C the temperature was decreased to 70°C. An aliquot sample indicated no isocyanate functionality remaining. The heating was stopped and the material was poured out of the reaction vessel into a container.

5 The additive bound oligomer was admixed with the diluent monomer Aronix M-113, adhesion promoter (MEMO), and the photoinitiator Lucirin TPO in a weight ratio of oligomer: Aronix M-113: MEMO: Lucirin TPO about 10 50.48:46.67:0.94:1.90 to produce a liquid composition of the invention. A film of this composition was cured using the "D" lamp. Differential Scanning Calorimetry of the cured film extracted with acetone showed essentially no change in OIT compared to the unextracted film. Thermogravimetric Analysis of the acetone 15 extracted film showed very little weight loss (1.14%) on heating at 200°C for 40 minutes.

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WE CLAIM:

1. A compound containing at least one polymerizable ethylenically unsaturated functional group and at least one stabilizer moiety covalently bonded within.

2. A polyurethane having at least one ethylenically unsaturated functional group and at least one stabilizer moiety, said urethane having a number average molecular weight of 1,000 to 10,000 daltons and being the reaction product of an isocyanate terminated prepolymer having a number average molecular weight of about 500 to 4,000 daltons, an equimolar mixture of a hydroxy terminated ethylenically unsaturated monomer and stabilizer compounds having a functional group capable of reacting with the isocyanate moiety.

3. The polyurethane of claim 2 wherein the stabilizer is N-(2,2,6,6-tetramethyl-4-piperidinyl)-N-hydroxybenzenepropionic hydrazide.

4. The polyurethane of claim 2 wherein the stabilizer is 3,5 ditertiary butyl-4-hydroxybenzenepropionic hydrazide.

5. The polyurethane of claim 2 wherein the stabilizers are both N-(2,2,6,6-tetramethyl-4-piperidinyl)-N-hydroxybenzene propionic hydrazide and 3,5 ditertiary butyl-4-hydroxy benzene propionic hydrazide.

6. The polyurethane of claim 2 wherein the hydroxy functional ethylenically unsaturated monomer is taken from the classes of acrylates, methacrylates, acrylamides, methacrylamides, maleates and vinyl ethers.

7. A coating composition that comprises: (i) about 10 to about 90% weight percent based on total weight of the coating composition, of an unsaturated polyurethane having a number average molecular weight of about 1,000 to about 10,000 daltons, being the reaction product of a prepolymer having a number average

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molecular weight of about 400 to about 2,000 daltons, a diisocyanate and a hydroxy functional unsaturated monomer, (ii) about 0.01 to about 25 weight percent, based on total weight of the coating composition, of a polyurethane having on at least one end an unsaturated moiety and on another end, the bound antioxidant, having a number average molecular weight of about 1,000 to about 10,000 daltons being the reaction product of an isocyanate terminated prepolymer having a number average molecular weight of about 500 to about 4,000 daltons, an equimolar mixture of hydroxy functional unsaturated monomer and an antioxidant containing a functional group capable of reacting with an isocyanate, (iii) about 0.01 to about 25 weight percent, based on the total weight of the coating composition of a polyurethane having on at least one end an ethylenically unsaturated group and on another, a bound light stabilizer moiety having a number average molecular weight of about 1,000 to about 10,000 daltons being the reaction product of an isocyanate terminated prepolymer having a number average molecular weight of about 500 to about 4,000 daltons, an equimolar mixture of hydroxy functional ethylenically unsaturated monomer and a light stabilizing compound having a functional group capable of reacting with an isocyanate group; and (IV) about 5 to about 80 weight percent, based on the total weight of the coating composition, of at least one unsaturated compound.

8. The coating composition of claim 7 wherein the stabilizer is N-(2,2,6,6-tetramethyl-4-piperidiny)-N-hydroxybenzenepropionic hydrazide.

9. The coating composition of claim 7 wherein the stabilizer is 3,5 ditertiary butyl-4-hydroxybenzene propionic hydrazide.

10. The coating composition of claim 7 wherein the stabilizers are N-(2,2,6,6-tetramethyl-4-

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piperdiny1)-N-hydroxybenzene propionic hydrazide and 3,5 ditertiary butyl-4-hydr xy benzen propi nic hydrazide.

11. The coating composition of claim 7 wherein the hydroxy functional ethylenically unsaturated monomers are taken from the classes of acrylates, methacrylates, acrylamides, methacrylamides, maleates and vinyl ethers.

12. The coating composition of claim 6 that further comprises a photoinitiator.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 91/00219

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08G18/67; C08G18/81; C08G18/10; C08G18/28
C08G18/38; C09D175/16

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	C08G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,4 128 536 (L.BRODSKY ET AL.) 5 December 1978 see claims 1-5,12 see figures 1-6 see column 1, line 47 - line 55 see column 2, line 31 - column 3, line 38 ---	1,2,6
X	US,A,4 504 628 (M.R.JOHNSON) 12 March 1985 cited in the application see claim 1 see column 3, line 15 - line 39 ---	1
A	FR,A,2 364 936 (BAYER) 14 Apr 11 1978 see claims 1,2,4 see page 5, line 25 - line 29 ---	1

¹⁰ Special categories of cited documents : ¹⁰^{"A"} document defining the general state of the art which is not considered to be of particular relevance^{"E"} earlier document but published on or after the international filing date^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)^{"O"} document referring to an oral disclosure, use, exhibition or other means^{"P"} document published prior to the international filing date but later than the priority date claimed^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"&"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

11 FEBRUARY 1992

Date of Mailing of this International Search Report

27 FEB 1992

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

VAN PUymbROECK M. A.

Van Puymbroeck

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. NL 9100219
SA 53617**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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FR-A-2364936	14-04-78	DE-A- 2642386 CA-A- 1109593 GB-A- 1559031 JP-A- 53039396 JP-B- 58029966 NL-A- 7710264 US-A- 4145512	23-03-78 22-09-81 09-01-80 11-04-78 25-06-83 23-03-78 20-03-79

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